A Comparison of Methods for
Calculating O(^{1}S) Lifetimes

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Abstract

It is shown theoretically and with simulated data that O(^{1}S) lifetimes determined by the cross-spectral method (Paulson and Shepherd 1965) are significant overestimates. A comparison is made of the cross-spectral and impulse function analysis (Burns and Reid 1984) methods using photometric data collected at Macquarie Island (54·5°S, 159·0°E geographic). The results support the view that the O(^{1}S) state is excited predominantly by an indirect process.

1. Introduction

The atomic oxygen O(^{1}S–^{1}D) 557·7 nm line emission is dominant in the auroral spectrum. It is this emission which often gives the aurora a green tinge. The pathway by which energy from incident auroral electrons is transferred to excitation of the O(^{1}S) state is still the subject of speculation.

The proposed excitation mechanisms may be classified as direct or indirect. Direct mechanisms result in the creation of the O(^{1}S) state simultaneously with the impact of the auroral electrons on the atmosphere. Electron impact excitation of atomic (Rees *et al.* 1967, 1969) and molecular (Donahue *et al.* 1968) oxygen are examples of direct excitation mechanisms. Indirect excitation mechanisms involve a metastable, or long-lived, intermediary in the creation of the O(^{1}S) state. Dissociative recombination of O_2^+ ions (Dalgarno and Khare 1967) and energy transfer from the $N_2(A^3\Sigma_u^+)$ state (Meyer *et al.* 1969; Parkinson and Zipf 1970; Parkinson 1971) are examples of indirect excitation mechanisms.

A number of calculations combining *in situ* measurements of various species with atmospheric models and laboratory determined reaction rate constants have been made in an attempt to determine the relative contributions of various possible mechanisms (Rees *et al.* 1977; Sharp and Torr 1979; O'Neil *et al.* 1979). The disparity between results obtained indicates the uncertainties inherent in these calculations.

The O(^{1}S) state is metastable with a theoretical radiative lifetime of 0·8 s (Nicolaides *et al.* 1971). In the auroral atmosphere, the effective lifetime of the O(^{1}S) state is reduced by collisions with other species which de-excite the state without radiation of a photon, a process known as collisional quenching. The greater the quenching of the O(^{1}S) state, the more O(^{1}S) states must be excited to yield a given measured

557·7 nm intensity. A knowledge of O(^{1}S) quenching rates is therefore required when investigating proposed excitation processes. Slanger and Black (1976) published laboratory results indicating that the O(^{1}S) state is expected to be significantly quenched in the auroral atmosphere by collisions with ground state atomic oxygen. However, they subsequently reported (Slanger and Black 1981) that atomic oxygen is not a significant quenching agent. This indicates the desirability of a procedure for measuring O(^{1}S) quenching rates independent of laboratory measurements which are difficult to perform.

A comparison of the intensity variations of the 557·7 nm emission with an emission accepted as being excited by a direct process (generally one of the N$_2^+$ 1NG band emissions is chosen) can be used to estimate the effective lifetime of the O(^{1}S) state (Omholt and Harang 1955). Paulson and Shepherd (1965) introduced a cross-spectral method to calculate the O(^{1}S) effective lifetime from digital photometric time series. This method has occasionally yielded unacceptable results with estimated O(^{1}S) effective lifetimes in excess of the radiative lifetime of the species (Brekke and Henriksen 1972).

In the general application of the cross-spectral method the assumption is made that only direct processes are responsible for the excitation of the O(^{1}S) state. Brekke and Pettersen (1972) and Brekke (1973) have adapted the cross-spectral method to search for indirect excitation processes. Although this process should yield adequate results, the effective lifetime values calculated for the proposed intermediate species are too long for the processes inferred to be accepted as significant contributors to the O(^{1}S) excitation.

In the present paper, O(^{1}S) effective lifetimes calculated from Macquarie Island data using the cross-spectral method (Paulson and Shepherd 1965) are compared with results obtained using an impulse function analysis procedure (Burns and Reid 1984) on the same data. The comparison shows that the cross-spectral technique overestimates the O(^{1}S) effective lifetimes. It should be noted that plotting the cross-spectral phase against the frequency as used in the cross-spectral technique and plotting the impulse function of the O(^{1}S–^{1}D) emission as used in the impulse analysis procedure are mathematically equivalent; they are Fourier transforms of each other. Where the application of the cross-spectral technique, as developed by Paulson and Shepherd, breaks down is if the O(^{1}S) state is not directly excited. The effects of an indirect process on the results of the cross-spectral method are first investigated theoretically. A comparison of theoretically derived plots of the cross-spectral phase against frequency with the plots of the Macquarie Island data is also made.

2. Mathematical Relationships

If the excitation rate of O(^{1}S) is instantaneously proportional to the energy flux of electrons incident on the atmosphere, and the lifetime of the O(^{1}S) state is constant throughout the emitting region, then a linear differential equation relates the O(^{1}S–^{1}D) 557·7 nm line emission and the N$_2^+$ 1NG 427·8 nm band emission (Omholt and Harang 1955):

$$\frac{\mathrm{d}I_O(t)}{\mathrm{d}t} + \frac{I_O(t)}{\tau} = k I_N(t),\tag{1}$$

where $I_O(t)$ and $I_N(t)$ are the intensities of the 557·7 and 427·8 nm emissions

respectively, τ is the effective lifetime of the O(^{1}S) state and k is a constant of proportionality.

Paulson and Shepherd (1965) showed that if equation (1) is valid, then the Fourier transform of the cross-correlation function between the two emissions $f_{on}(\omega)$, and the Fourier transform of the auto-correlation function of the N$_2^+$ 1NG band $f_{nn}(\omega)$, are related by the equation

$$f_{on}(\omega) = \frac{\sigma_n}{\sigma_o} \frac{k\tau(1 - i\,\omega\tau)}{1 + \tau^2\omega^2} f_{nn}(\omega),\tag{2}$$

where σ_n and σ_o are the standard deviations of the N$_2^+$ 1NG (427·8 nm) and 557·7 nm time series respectively. This implies that the tangent of the cross-spectral phase $\phi_{on}(\omega)$ is linearly related to the frequency:

$$\tan\{\phi_{on}(\omega)\} = -\omega\tau.\tag{3}$$

A number of indirect processes have been proposed for excitation of the O(^{1}S) state. As already mentioned, the energy transfer reaction

$$N_2(A^3\Sigma_u^+) + O(^3P) \rightarrow N_2(X^1\Sigma_g^+) + O(^1S),$$
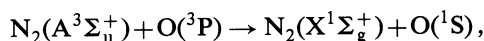
and the dissociative recombination reaction

$$O_2^+ + e \rightarrow O(^1S) + O(^3P)$$
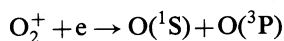
are examples of indirect excitation reactions. If the excitation of the time dependent species involved in the indirect excitation reaction is proportional to the energy of the incident electrons, then equation (1) can be replaced by

$$\frac{dI_O(t)}{dt} + \frac{I_O(t)}{\tau} = K_1 I_N(t) + K_2 X(t),\tag{4}$$

$$\frac{dX(t)}{dt} + \frac{X(t)}{\tau'} = K_3 I_N(t),\tag{5}$$

where $X(t)$ is the time dependent concentration of the species involved in the indirect excitation process, τ' is the lifetime of this species and K_1, K_2, and K_3 are constants of proportionality (Parkinson 1971; Henriksen 1973).

Brekke and Pettersen (1972) have calculated the relation between the Fourier transforms of the cross-correlation function and the auto-correlation function if the O(^{1}S) state is excited in the manner described by equations (4) and (5). The relevant equation is now

$$f_{on}(\omega) = \frac{\sigma_n}{\sigma_o} \frac{K_2 K_3 + K_1(\tau'^{-1} + i\,\omega)}{(\tau^{-1} + i\,\omega)(\tau'^{-1} + i\,\omega)} f_{nn}(\omega).\tag{6}$$

Burns and Reid (1984) described a method for evaluating the impulse function relating the $O(^1S-^1D)$ (557·7 nm) and N_2^+ 1NG (427·8 nm) time series.* If equations (4) and (5) hold, then the impulse function $g(t)$ will be of the form

$$g(t) = A' \exp(-t/\tau) - B' \exp(-t/\tau'),\qquad(7a)$$

where

$$A' = K_1 + K_2 K_3 \frac{\tau'\tau}{\tau-\tau'},\qquad B' = K_2 K_3 \frac{\tau'\tau}{\tau-\tau'}.\qquad(7b, c)$$

We consider the case in which the $O(^1S)$ state is excited solely by an indirect process. This implies $K_1 = 0$ in equation (4), and equation (6) reduces to

$$f_{on}(\omega) = \frac{\sigma_n}{\sigma_o} \frac{K_2 K_3}{(\tau^{-1}+i\omega)(\tau'^{-1}+i\omega)} f_{nn}(\omega).\qquad(8)$$

The cross-spectral phase is thus related to the frequency by the equation

$$\tan\{\phi_{on}(\omega)\} = -\omega(\tau+\tau')/(1-\omega^2\tau\tau').\qquad(9)$$

Expanding this for $\omega^2\tau\tau' \ll 1$ gives

$$\tan\{\phi_{on}(\omega)\} = -\omega(\tau+\tau')\{1+\omega^2\tau\tau'-\tfrac{1}{2}(\omega^2\tau\tau')^2+\ldots\}.\qquad(10)$$

In practice, when plotting $\tan\{\phi_{on}(\omega)\}$ against ω it is found that a linear relationship holds out to a particular frequency, above which noise forms a considerable fraction of the spectral densities $f_{on}(\omega)$ and $f_{nn}(\omega)$ and the relationship breaks down. Equation (10) implies that calculating the gradient in this fashion, if the $O(^1S)$ state is indirectly excited, will yield $\tau+\tau'$ in the limit of small ω. The first correction term $\omega^3\tau\tau'(\tau+\tau')$ varies as the cube of the frequency, and will increase the estimated value of $\tau+\tau'$ if a linear fit is applied.

A 5-minute time series of N_2^+ 1NG (427·8 nm) emission, sampled at the rate of 10 Hz, was convolved with an impulse function of the form

$$g(t) = e^{-t/0.7} - e^{-t/0.1},\qquad(11)$$

where t is measured in s. This yields test data corresponding to a time varying 557·7 nm emission for which the $O(^1S)$ state is indirectly excited by a process, for which $\tau' = 0.1$ s, and for which the effective $O(^1S)$ lifetime is 0·7 s.

Fig. 1 shows a plot of $\tan\{\phi_{on}(\omega)\}$ against ω using these time series as inputs. Also shown is the coherency given by

$$\gamma_{on}(\omega) = |f_{on}(\omega)|/\{f_{nn}(\omega)f_{oo}(\omega)\}^{\frac{1}{2}}.\qquad(12)$$

A straight line fitted to 0·17 Hz yields a gradient of 0·98 s.

The 427·8 nm data were also convolved with a single exponential function having

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* Burns and Reid (1984) contains the following errors: For consistency with the development presented in that paper, A in their equation (1) should be replaced by $A\tau$, K in equation (3) by $K\tau$, and K' in equation (4) by $K'\tau'$.
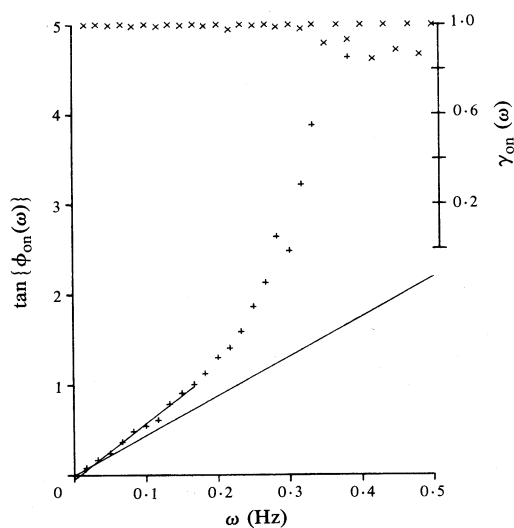
Fig. 1. Cross-spectral analysis for constructed data (with $\tau = 0.70$ s and $\tau' = 0.1$ s). A linear fit to 0.17 Hz yields a gradient of 0.98 s, whereas the lower line represents a 0.70 s gradient.
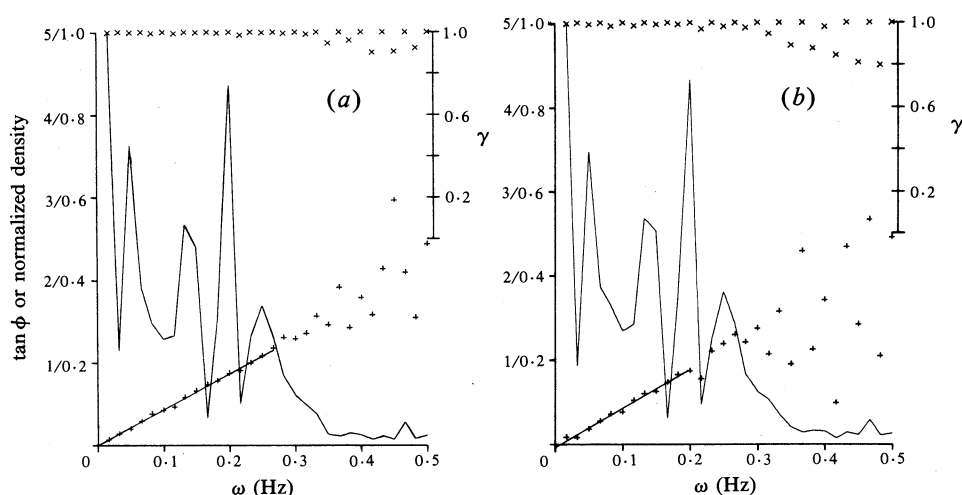

Fig. 2. Cross-spectral analysis using (*a*) test data generated by convolving a 427·8 nm time series with a 0·7 s exponential decay. A linear fit to $\omega = 0.267$ Hz yields a 0·69 s gradient. The curve represents the normalized 427·8 nm spectral density $|f_{nn}(\omega)|$. (*b*) As for (*a*) but with noise added to the 427·8 nm time series. A linear fit to 0·2 Hz yields a gradient of 0·74 s.

a 0·7 s decay. This serves as 'direct excitation' 557·7 nm test data. Fig. 2*a* displays the results obtained using these time series as inputs. A straight line least-squares fit to the data out to 0·267 Hz yields a 0·69 s gradient. Fig. 2*b* is the result obtained when white noise, amplitude limited to 20% of the range of the initial data, is added to the 427·8 nm time series. Fitting a straight line out to 0·2 Hz yields a 0·74 s gradient. Note that the effect of noise on the data is to generate a greater spread in $\tan\{\phi_{on}(\omega)\}$ values, but that the linear trend is maintained. For the generated indirect excitation data (Fig. 1) an increasing deviation from the linear fit is apparent.
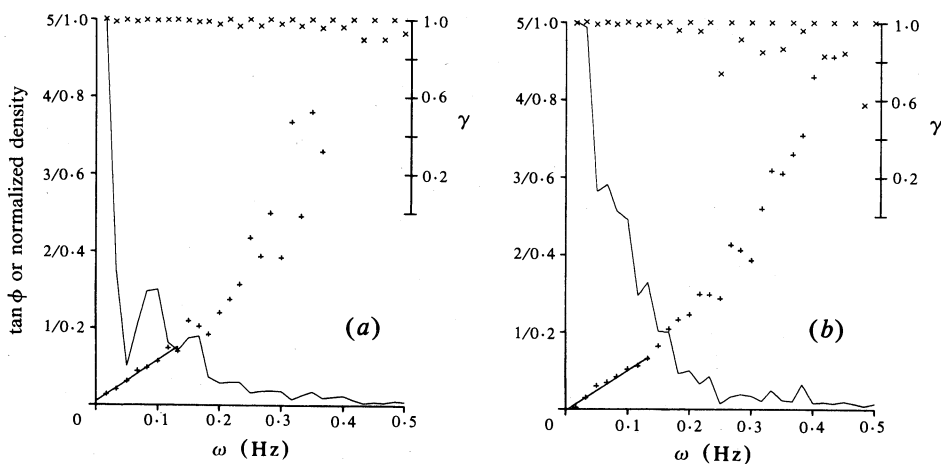
Fig. 3.   Cross-spectral analysis for the Macquarie Island data: (a) 1740–1745 UT, 21/7/80, $\tau = 0\cdot85$ s; (b) 1540–1545 UT, 18/8/80, $\tau = 0\cdot82$ s.

3. Comparison of Methods

Figs 3a and 3b show respectively the plots obtained from 5-minute 427·8 and 557·7 nm data samples collected by a twin channel wide-angle (30° half-angle) zenith oriented photometer system at Macquarie Island (geographic coordinates 54·5°S, 159·0°E; geomagnetic invariant coordinates, epoch 1977·25, 64·5°S, 177·7°E). The similarity of these plots to the constructed indirect excitation data in Fig. 2 is readily apparent.

Burns and Reid (1984) have carried out similar tests on the impulse function analysis method. The method of determining the $O(^1S)$ lifetime is to fit a twin exponential of the form given by equation (7a) to the calculated impulse functions. Fig. 4 shows the impulse functions calculated for the Macquarie Island data used in the cross-spectral analysis. The pure exponential decay away from the zero time of the impulse and the rounding of the impulse near $t = 0$ are indicative of the short lifetime associated with the indirect process. The $O(^1S)$ effective lifetime is calculated by fitting a least-squares best fit exponential decay to 15 consecutive points of the impulse functions. The first five points after the zero time of the impulse function are then subtracted from the calculated exponential decay. The decay time of the indirect process is calculated from these points and an iterative procedure is used to obtain a best fit (Burns and Reid 1984). From the values of K_1 and $K_2 K_3$ (equations 7b and 7c), calculated for the best fit of the impulse function, the relative contribution of the indirect process to the excitation of the $O(^1S)$ state can be calculated.

The $O(^1S)$ effective lifetimes calculated by the cross-spectral method, for the data presented, are 0·85 and 0·82 s. Using the impulse function analysis, the $O(^1S)$ lifetimes calculated are 0·65 s with 80% indirect excitation from a 0·13 s decay time process (Fig. 4a), and 0·70 s with 70% indirect excitation from a 0·10 s decay time
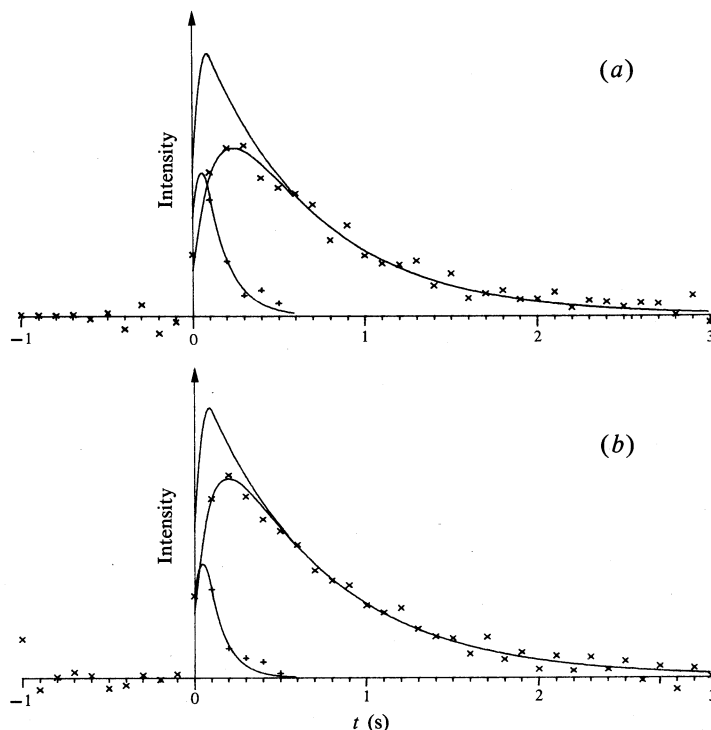
Fig. 4. Impulse function analysis for the Macquarie Island data: (*a*) 1740–1745 UT, 21/7/80, $\tau = 0 \cdot 65$ s, $\tau' = 0 \cdot 13$ s, 80% indirect excitation; (*b*) 1540–1545 UT, 18/8/80, $\tau = 0 \cdot 70$ s, $\tau' = 0 \cdot 10$ s, 70% indirect excitation. With the nomenclature of equation (7a), the top curve in each case is $A' \exp(-t/\tau)$, the middle curve is $A' \exp(-t/\tau) - B' \exp(-t/\tau')$ and the bottom curve is $B' \exp(-t/\tau')$. The crosses give the measured impulse response and the plusses give the difference between the $A' \exp(-t/\tau)$ term and the measured impulse. The fits depart from true exponentials for $t < 0 \cdot 1$ s as a result of sampling rate limitations.

process (Fig. 4*b*). A comparison of the cross-spectral analysis of the constructed data (Fig. 1) and the real data (Figs 3*a* and 3*b*) supports the calculated result of a large contribution from an indirect excitation process.

Eighteen 5-minute data samples collected at Macquarie Island were selected for a comparison of the cross-spectral and impulse function methods of determining the O(^{1}S) lifetime. These samples were selected on the basis that the calculated impulse function indicated that the data have a good signal-to-noise ratio, and that the background variations in the two emissions were insignificant (Burns and Reid 1984). Of these 18 data samples, there were two for which a linear fit was a poor approximation to the $\tan\{\phi_{on}(\omega)\}$ versus ω plot, and one for which the twin exponential fit yielded decay times approximately equal. A comparison of the results obtained using the remaining 15 samples is shown in Table 1. In all but one of these samples the impulse analysis technique yielded a shorter lifetime than the cross-spectral technique. The average difference between the estimates calculated

using the two methods is 0.11 s. A comparison of estimated lifetimes from successive 5-minute data samples from a larger data set yields a standard deviation of ± 0.05 s on the impulse function analysis estimates (Burns and Reid 1984).

Table 1. Comparison of the $O(^1S)$ effective lifetimes estimated by the cross-spectral and impulse analysis techniques

Date (1980)	Time (UT)	Cross-spectral technique (s)	Impulse technique (s)
12/5	1835–1840	0·91	0·71
7/6	1735–1740	0·74	0·58
10/6	1750–1755	0·82	0·62
10/6	1755–1800	0·72	0·67
12/6	1905–1910	0·77	0·63
7/7	1610–1615	0·92	0·78
21/7	1740–1745	0·85	0·65
18/8	1530–1535	0·96	0·74
18/8	1535–1540	0·80	0·79
18/8	1540–1545	0·82	0·70
9/8	1645–1650	0·69	0·76
9/9	1730–1735	0·79	0·75
11/9	1625–1630	0·78	0·76
9/10	1650–1655	0·72	0·68
9/10	1655–1700	0·89	0·68
Mean and standard deviation		0·81±0·08	0·70±0·06

4. Discussion

In introducing the cross-spectral Fourier analysis method, Paulson and Shepherd (1965) noted that the departure of the $\tan\{\phi_{on}(\omega)\}$ plots from linearity often occurred at frequencies for which the coherency of the emissions was still high. In four of the six samples they examined, a second linear relation with a different slope was apparent. Scourfield *et al.* (1971) also noted this effect. Figs 3*a* and 3*b* may be interpreted in this manner. It was suspected that this behaviour signified an indirect excitation process and it has been shown here that this is correct. It has also been shown that a significant contribution from an indirect excitation process leads to considerably higher $O(^1S)$ lifetime estimates than are correct.

The advantage of using the impulse function analysis technique is that, if short effective lifetime indirect processes are involved in exciting the $O(^1S)$ state, the effective lifetime of the $O(^1S)$ species may be estimated by fitting an exponential to points away from the impulse zero time.

Brekke and Henriksen (1972) calculated the $O(^1S)$ lifetime from 735 5-minute samples of data using the cross-spectral Fourier transform method and derived a mean effective lifetime of 0.8 s. A significant number of lifetime estimates with values greater than 1.0 s were obtained, at variance with theoretical estimates of the radiative lifetime of the $O(^1S)$ state. The theoretical calculations of Nicolaides *et al.* (1971) imply a radiative lifetime of 0.80 s.

Brekke and Pettersen (1972) and Brekke (1973) analysed their data set for evidence of indirect excitation of the $O(^1S)$ state. The average lifetimes calculated for the assumed species involved in the indirect excitation process were 1–20 s associated with

the O_2^+ ion (Brekke and Pettersen 1972) and $0\cdot4$–$0\cdot65$ s for the $N_2(A^3\Sigma_u^+)$ species (Brekke 1973). These results were obtained by a least-squares fitting of equation (6) to the $f_{on}(\omega)$ calculations, a method mathematically equivalent to the impulse analysis procedure. It is difficult to accept significant contributions from indirect processes with lifetimes of this magnitude given the closeness with which the $557\cdot7$ nm line emissions are observed to follow the N_2^+ 1NG emissions. Burns and Reid (1984) have shown that adding amplitude limited white noise to the input time series, or a variation such that the time series are not related by a linear filter, may yield inaccurate results. The data reduction technique adopted by Burns and Reid (1984) rejected data contaminated in this manner. The unacceptably large indirect process lifetimes calculated by Brekke and Pettersen (1972) and Brekke (1973) may therefore result from inadequate data selection techniques.

Several authors have calculated the percentage contribution of the various excitation processes of the O(^{1}S) state using rocket and/or satellite measurements of the relevant atmospheric constituents (Arnoldy and Lewis 1977; Sharp *et al.* 1979; O'Neil *et al.* 1979; Sharp and Torr 1979). In these studies a measured $557\cdot7$ nm emission was compared with that calculated from the measured concentration of the atmospheric species and laboratory determined rate constants. There is general support for a large contribution from indirect processes to the excitation of the O(^{1}S) state. There is however some doubt as to the validity of the rate constants used in these calculations. Slanger and Black (1981) reported that the generally accepted quenching rate of O(^{1}S) by O(^{1}P) is a significant over-estimation. Bates and Zipf (1980) have stressed some puzzling aspects of the O(^{1}S) yield in O_2^+ dissociation recombination. The present paper provides further evidence for a high degree of indirect excitation of the O(^{1}S) state, independent of the reaction rate constants.

Acknowledgments

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